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I, LEANNE MYNOTT, MANAGER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. 2003906427 for a patent by THE UNIVERSITY OF QUEENSLAND as filed on 21 November 2003.



WITNESS my hand this
Eighth day of December 2004

A handwritten signature in dark ink, appearing to be 'A' or 'L' with a flourish.

LEANNE MYNOTT
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AND SALES

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AUSTRALIA

Patents Act 1990

PROVISIONAL SPECIFICATION

**Invention Title: "SILICA FILMS AND METHOD OF
PRODUCTION THEREOF"**

The invention is described in the following statement:

SILICA FILMS AND METHOD OF PRODUCTION THEREOF

FIELD OF INVENTION

THIS INVENTION RELATES to silica films, a method of production thereof and the use of the silica films as anti-reflective and/or anti-fogging coatings. In particular the invention relates to silica films having a refractive index lower than pure silica.

BACKGROUND

Typically low refractive index thin films are made utilising sol-gel processes or vacuum evaporation deposition techniques. The following prior art documents are but a few examples of methods used to produce silica films.

WO 02/41043 is directed to a method of forming a meso-structured inorganic/block copolymer composite or inorganic porous solid doped with a dye or dye sensitive agents, formed by creating a silica sol-gel from tetraethoxysilicate (TEOS), ethanol and water. The sol-gel is then polymerized with block copolymers, such as poly(ethylene oxide)-poly(alkylene oxide)-poly(ethylene oxide). The inorganic/organic composite is then calcined or subjected to solvent extraction to remove excess block copolymer species, prior to doping with dye/dye sensitive agents.

US 6,379,776 is directed to a multi-layer, anti-fogging and stain preventing glass coating comprising an alkaline shut-off film, a silica oxide/zirconium oxide composite, and a photocatalytic film, of titanium oxide. Both the silica oxide/zirconium oxide composite layer and the titanium oxide layers are formed using known sol-gel processes.

US 2002/0090519 describes a method of hydrolytically polycondensating tetraalkoxysilanes to form a silica oxide sol. The hydrolytic polycondensation occurs by placing the tetraalkoxysilane in an aqueous alcohol ammoniacal solution to encourage hydrolysis of the tetraalkoxysilane and produce silica oxide particles. The sol is subject to steam distillation in order to remove the alcohol and ammonia prior to the pH being adjusted to between 3 and 8. Surfactants are then added to the silica sol to act as a pore templates during the coating of a substrate. The coating is calcined to cure the silica film and remove the surfactants.

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US 5,948,482 is directed to a method of forming an aerogel thin film at ambient pressure, by forming a silica oxide sol-gel using standard processes before derivatizing the surface of the gel with a hydrolisable organic substituent, reliquefying the sol with sonication and depositing the gel onto a substrate.

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US 5,698,266 is directed to a method of forming an anti-reflective sol-gel coating by mixing ethanol, tetraethoxysilicate (TEOS) and ammonia and hydrolysing for up to 48 hours. The silica sol is then filtered to obtain silica particles for deposition onto a substrate, prior to drying. The coated substrate is placed in an ammoniacal environment for up to twelve hours to form an anti-reflective coating.

C. Shelle et al, *J. Non-Cryst. Solids*, 218, pg 163, 1997, describes a method of producing anti-glare glass films using sol-gel coatings formed from methyltriethoxysilane, tetraethoxysilicate and tin oxide. The sol-gel is aged at 0°C prior to deposition onto a substrate and calcining at 500°C.

G Wu, et al, *J. Non-Cryst. Solids*, 275, pg 169, 2000, describes a method of creating a sol-gel, in which tetraethoxysilicate (TEOS) is catalysed in a two step acid-base process. The TEOS is initially aged in an ammonia-ethanol solution, pH adjusted, refluxed and a second pH adjustment made.

5 In preparing the films, G. Wu et al deposit the sol-gel onto a substrate and cure in an ammoniacal environment.

Hass D. D. et al, NASA Contractor Report, 201733, teaches the coating of fibrous insulation with a reflective film such as silica, titanium dioxide, zirconium oxide and/or combinations thereof. The oxides are formed
10 using known sol-gel processes into which the fibrous insulation is submersed to coat the fibres prior to vacuum or heat drying.

The above processes which rely on sol-gel techniques for producing thin films are complex, multi-step processes which are costly, involve high temperature steps in fabrication, and/or require a surfactant for templating.
15 The films produced by sol-gel processes are typically easy to damage and/or liable to delamination.

SUMMARY OF THE INVENTION

In one form, although it need not be the only or indeed the broadest form, the invention resides in a method of forming a silica film coated
20 substrate including the steps of;

producing a silica precursor formulation by adding silicic acid tetramethyl ester homopolymer and tetramethoxysilane to an aqueous-alcohol solution;

coating a substrate with the silica precursor formulation; and

curing the silica precursor formulation onto the substrate.

The curing step of the above method may be carried out by placing the coated substrate in a closed ammoniacal environment.

Preferably the silica precursor formulation is formed by adding methyl-
5 silicate-51 (MS-51), comprising >94% silicic acid tetramethyl ester homopolymer, <3% tetramethoxysilane and <3% methanol; to an aqueous-alcohol solution.

The silica precursor formulation may comprise about 0.01-1 parts water and 0.01-100 parts alcohol for each part of MS-51. Preferably the
10 silica precursor formulation comprises about 0.01 to 15 parts alcohol and 0.01 to 1 part water for each part of MS-51. More suitable the ratio of reagents in the silica precursor formulation are 1.0 part MS-51: 0.1 part water: 6.0 parts alcohol.

Another form of the invention provides a method of forming a silica
15 precursor formulation, including the step of;

adding silicic acid tetramethyl ester homopolymer and tetramethoxysilane to an aqueous-alcohol solution.

The invention also provides a silica precursor formulation comprising;
about 1 part including >94% silicic acid tetramethyl ester
20 homopolymer and <3% tetramethoxysilane;
about 0.01-100 parts alcohol; and
about 0.01-1 part water.

In another form the invention provides a silica film having a refractive index between 1.1 and 1.56 and a film thickness less than 100 microns

formed by the method including the steps of;

producing a silica precursor formulation by adding silicic acid tetramethyl ester homopolymer and tetramethoxysilane to an aqueous-alcohol solution;

- 5 coating a substrate with the silica precursor formulation; and
 curing the silica precursor formulation onto the substrate.

In yet another form the invention provides for the use of the silica film, described above, to coat transparent substrates to provide an anti-reflective and/or anti-fogging coating.

- 10 Throughout the specification the term "low refractive index" is intended to refer to a silica film of the invention having a refractive index less than 1.56 in the visible range.

BRIEF DISCRIPTION OF DRAWINGS

- FIG. 1 is a graph of the UV-visible optical transmission spectrum of the
15 film of Example 1.
- FIG. 2 is a graph of the UV-visible optical transmission spectrum of a
 spin coated film of silica on glass produced by the method of the
 invention.
- FIG. 3 is a UV-visible optical transmission spectra for an uncoated glass
20 slide and a glass slide coated with an anti-reflective silica film
 formed by the method of the invention.

DETAILED DESCRIPTION OF THE INVENTION

Example 1:

10ml of methyl-silicate-51 (comprising silicic acid tetramethyl ester

homopolymer >94%, tetramethoxysilane <3%, methanol <3%) { supplied by COLCOAT CO. LTD. 3-28-6 Omorinishi, Ota-ku, Tokoyo 143-0015, Japan} is added to solution of 60ml ethanol or methanol, and 1ml water to form a silica precursor formulation.

- 5 The silica precursor formulation may comprise any alcohol that creates dispersed droplets throughout the silica precursor formulation and facilitate the formation of pores in the final film.

 The precursor solution is applied to a substrate, in this example a glass slide, by spin coating at a spreading time = 1s, spreading speed =
10 500rpm, ramp = 500rpm/s, spin time = 1s, spin speed = 2500, ramp = 2500rpm/s.

 It will be appreciated that spin deposition conditions may be varied depending on the film thickness and refractive index desired. Other deposition techniques such as dip coating and spraying may also be used to
15 apply the silica precursor formulation to a substrate.

 The coated substrate is then place in a closed container containing a curing agent (2.5ml ammonia, 7.5ml water and 20ml alcohol), which creates an appropriate ammoniacal atmosphere for the silica film to cure. The container is arranged in such a manner that the film is never in contact with
20 the curing liquid. This curing step continues until the film solidifies and becomes mechanically robust.

 It will be appreciated that any quantities of water, alcohol and ammonia/ammonium hydroxide may be used to create the ammoniacal atmosphere to cure the silica film.

The silica films of this example, and produced in a similar manner to this example, were physically characterised. The results of the physical characterisation are summarised below.

Optical transparency

5 The optical transparency of the film of Example 1, and similar films was determined using a Perkin Elmer Lambda 40 UV-Visible Spectrophotometer, having the following scan settings:

	Slit width	2nm,
	Scan speed	240nm/min,
10	Data interval	1nm.

An empty sample arm was used to determine the background spectra for correction purposes.

15 The UV-Visible optical transmission spectrum was measured for the thin film (film thickness of less than 2 microns) of Example 1. The spectrum is shown in FIG. 1. The key feature of these spectra is the high optical transmission of the coated glass substrate over the entire visible spectrum. This observation may also be confirmed by simply looking at the coated glass substrate which appears transparent to the eye.

20 FIG 2 is a UV-Visible optical transmission spectrum for a silica film, having a film thickness of approximately 4 microns, formed in a similar manner to Example 1. The film used for this test was thicker than that used in FIG.1 evidenced by the interference fringes, peaks and troughs, as a function of wavelength. The fringe contrast is appreciable (~5%), indicating that the refractive index of the film is <1.3 .

Scratch resistance

The hardness test or scratch resistance test was conducted by taking a set of pencils ranging in hardness from 2B (soft) to 7H (quite hard) and attempting to scratch the film's surface of Example 1. None of these pencils
5 were able to scratch the material, leading to the conclusion that the material hardness is $> 7H$ on the pencil scale.

These hardness and scratch resistance results indicate that the films of the current invention are similar to glass and significantly better than vacuum coated dielectric low refractive index coatings.

10 Solvent resistance

The films were found to be resistant to water, alcohols, common acids and alkalis.

Anti-fogging

The silica films formed by the method of Example 1 have been found
15 to provide effective anti-fogging properties. The porosity or surface area of the silica films is approximately $150\text{m}^2/\text{g}$, using standard nitrogen adsorption-absorption techniques. It is believed that coatings having a minimum surface area of $10\text{m}^2/\text{g}$ will exhibit anti-fogging properties.

It is believed that the anti-fogging properties of the silica films of the
20 invention are due to the hydrophilicity and high surface area of the films. It is thought that the high surface area and hydrophilicity of the films allows atmospheric water to be absorbed onto the film, thus preventing water droplets from forming.

Example 2:

Another silica film was formed in a manner similar to Example 1. To compare the features of the silica film of this example with that of its substrate, a glass slide, UV-visible optical transmission spectra was recorded for both a coated substrate and uncoated substrate, shown in FIG 3.

5 Ordinarily, ~4% of incident light is reflected from each glass-air interface, leading to a normal transmission of ~92% for an uncoated glass substrate. FIG. 3 shows the increase (~94.6%) in transmission that can be achieved by coating one side of a glass substrate with a low refractive index film produced by the new process. Theoretically, a thin film of refractive
10 index ~1.22, and of an appropriate thickness, would be the perfect anti-reflective coating for glass, as it would have a 96% transmission for a single sided coating. This transmission value is very close to the experimental value. Showing that the films of the current invention are effective anti-reflective coatings for glass.

15 Example 3

A substrate, for example a mirror, is sprayed with the silica precursor formulation. An aqueous ammonia solution is sprayed over the silica precursor formulation. The silica precursor is allowed to cure at room temperature forming a silica film.

20 The silica thin films produced by this method have been found to have a number of favourable characteristics, including:

a low refractive index in the visible spectrum, typically 1.1 to 1.56;

high optical transparency;

25 high optical and thickness uniformity;

mechanical robustness similar to glass;
chemical and photochemical properties similar to glass;
high porosity, leading to efficient anti-fogging behaviour;
excellent adhesion to conventional substrates, such as glasses,
5 plastics, metals, ceramics, semiconductors, and the like; and
durability / long term stability.

A number of features of the silica films of the current invention may be
tailored or tunable to suit the final application of the film, for example;

10 Tunable refractive index - The refractive index may be tuned
according to need by adjusting the composition, in particular the
alcohol and water content.

Tunable film thickness - The film thickness can be tuned by adjusting
the initial alcohol and water contents in the precursor formulation and,
can also be adjusted by varying the parameters relating to the
15 deposition method, such as spin speed, viscosity, dip coating
withdrawal rate, and the like.

The viscosity of the silica precursor formulation may be altered to
facilitate its use in a range of applications, for example a highly viscous
formulations may be formed so that when sprayed onto a substrate to create
20 a thin coverage of the precursor the surface attraction of the precursor to the
substrate is greater than the effects of gravity, thus preventing the precursor
from running whilst curing.

The method of the current invention provides a low cost simple
method for producing robust films with effective control over the thickness

and refractive index of the coating, along with being able to coat a range of substrate shapes.

5 The above properties make the films ideal candidates for cheap, robust, efficient optical coatings for applications including antireflection coatings, chemical and mechanical barrier coatings, anti-fogging coatings, anti-glare coatings (light diffusing effect), high reflectivity coatings, low refractive index supports and cladding and dielectric barrier layers.

10 The silica thin films of the invention may be employed as low refractive index optical coatings for anti-reflection coatings or as a low refractive index material in high-low refractive index multilayer coatings. As a low refractive index optical coating the silica thin films may be applied to all forms of glass including spectacles, windows, windscreens, decorative, etc.; coatings for CRT and other display devices such as computer monitors, televisions, etc.; coatings for solar cells; optical instrument coatings such as
15 lenses, mirrors, and the like; active and passive optical waveguides in telecommunications, and advanced photonics; and optoelectronic devices.

 The silica thin films may also be used as physical and chemical barrier coatings including, invisible metal and plastics protection, invisible protection for delicate optical surfaces.

20 The silica thin films may also be used as anti-fogging coatings for applications including automotive and marine glass, architectural glass, spectacles, windows of all sorts, bathroom mirrors and shower screens.

 It will be appreciated by the person skilled in the art that the above films may be formed on or applied to glass surfaces that are already in place,

such as existing windows and mirrors. In aftermarket applications the silica precursor formulation may be mixed with the curing agent immediately prior to application, mixed during application such as through a common spray nozzle or after the silica precursor has been applied to a substrate.

- 5 Alternatively the silica precursor may be applied to a substrate and allowed to cure under ambient conditions, without the addition of any curing agent. The silica precursor and/or curing agent may be applied by coating, wiping or spraying the respective component onto the substrate being treated. The curing agent may be any gaseous or aqueous strong alkali, including
10 ammonia, alkali metal hydroxides, quaternary alkyl ammonium hydroxides and the like.

Throughout the specification the aim has been to describe the preferred embodiments of the invention without limiting the invention to any one embodiment or specific collection of features.

- 15 Throughout this specification, unless the context requires otherwise, the word "comprises", and variations such as "comprise" or "comprising", will be understood to imply the inclusion of a stated integer or group of integers or steps but not to the exclusion of any other integer or group of integers.

DATED this the twenty first day of November 2003.

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THE UNIVERSITY OF QUEENSLAND

By Their Patent Attorneys

FISHER ADAMS KELLY

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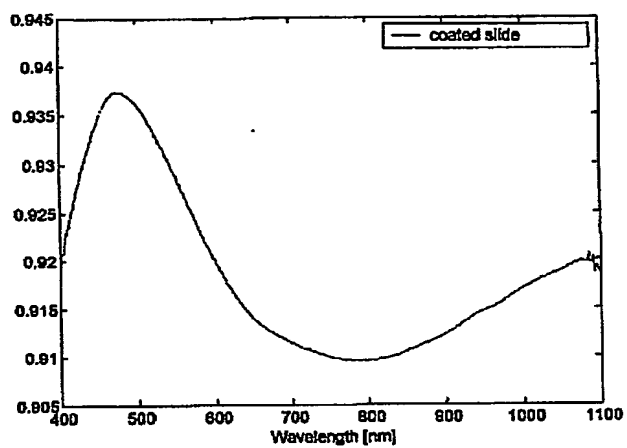


FIG 1

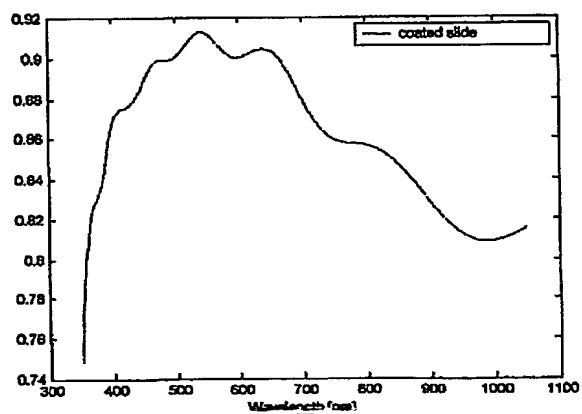


FIG 2

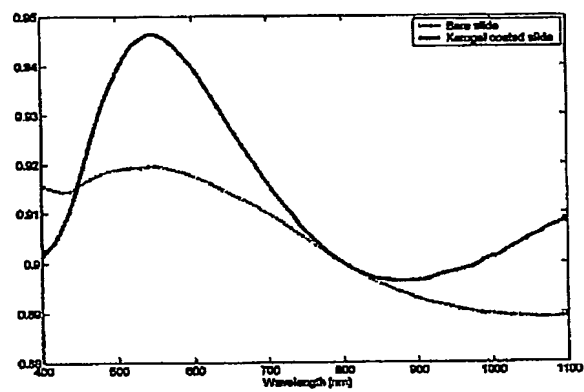


FIG 3

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